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- "3. So large a proportion of the mental derangements of women being sympathetic and reflex, and referable to local derangements, herein differing from what obtains in men, where insanity is more frequently of centric and cerebral origin, there is decided indication for local curative treatment much oftener than it is now resorted to in cases of insane women, either at asylums or in private practice."
- Dr. Storer presented various evidence corroboratory of his views, and related an illustrative case. He also alluded to a peculiar sensational torpor of the insane as explanatory of the otherwise unaccountable fact that severe physical lesions, as fracture of ribs, &c., are not unfrequently discovered at postmortem examinations of the insane, of which no complaint or suspicion had existed during life. From this he drew another deduction of practical importance in the administration of criminal law.
- "4. In medico-legal investigations, whether they are coroner's inquests, trials for homicide, or for the abuse of insane patients in confinement, it must not be forgotten that the insane, so far as regards matters of sensation, whether as to effects from wounds or from acute or chronic disease, are not to be judged by the ordinary physiological laws."

## Five hundred and thirty-second Meeting.

March 8, 1864. — MONTHLY MEETING.

The President in the chair.

The President called the attention of the Academy to the recent decease of three of its members; viz. Professor Edward Hitchcock of the Resident Fellows, and Baron Plana and Heinrich Rose of the Foreign Honorary Members.

The following papers were presented.

- On the Right Ascension of the Pole Star, as determined from Observation. By Truman Henry Safford, Assistant at the Observatory of Harvard College.
- 1. The fixed star a Ursæ Minoris, the Pole-Star, has been the object of very numerous observations, more indeed than any other celes-

tial body, except, perhaps, the sun, the moon, and the principal exterior planets.

The reason is, that all observers of the northern hemisphere must depend upon it in a great degree to assure themselves of the position of their instruments.

Not only has this star been much observed, but many of the observations have been made serviceable for the determination of its position; whatever accuracy is possible in the place of a star should characterize the place of this. Nevertheless, there does not seem to be perfect security about its right-ascension; the different predictions of it given in different places do not harmonize so well with each other; or with observation, as might, perhaps, be expected. Thus, for example, the fifty-two consecutive transits which I have observed at the Harvard College Observatory (with the Simms meridian circle), in pursuance of the definitive plan mentioned in the Report of Professor Bond for 1862 (pp. 24 – 26), give the star's mean right ascension for 1863.0,

or greater by 0°.81 than Wolfers's prediction in the Berliner Astronomisches Jahrbuch for that year, and greater by 1°.22 than that given in Dr. Gould's pamphlet, "Standard Places of Fundamental Stars, U. S. Coast Survey."

Reducing this back to 1860.0 by the proper motion now employed in the Jahrbuch, we have

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Cambridge Observations, 1860.0 1h 8m 3s.464

Wolfers " 2.654 Obs. — W. = +0s.81

Bessel - Zech (Jahrbuch for 1860) 2.799 Obs. — B. Z. = +0.66

Gould (for 1860) 2.32 Obs. — G. = +1.14
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2. So far, then, as my own observations go, the earlier prediction of Bessel, the elements of which were determined in 1826, is more accurate than either of the later ones. It remains now to examine other observations made lately, to see if they concur in the same conclusion. One observer's work may be, and probably is, affected by a personal equation. We will compare Dr. Gould's tables of A. R. of Polaris, which extend from 1851 to 1863, with the observations made at Greenwich, Paris, and Cambridge, England, so far as the volumes containing them have reached us. To this will be added a comparison with Bessel's Tabulæ Regiomontanæ, as continued from the same elements by Professor Zech.

Comparison of Dr. Gould's Table of A. R. of Polaris with Observations.

| ,             |       |              | <del></del> |         |             |         |
|---------------|-------|--------------|-------------|---------|-------------|---------|
|               | ¥     | Observed.    | Comp'd (G.) | o. — c. | Comp'd (Z.) | 0. — C. |
|               |       | hm s         | 8           | 5       | s           | 8.      |
| Greenwich     | 1851  | 1 5 19.02    | 18.66       | +0.36   | 18.91       | +0.11   |
| 0.100.1110.11 | 1852  | 36.75        | 36.37       | +0.38   | 36.64       | +0.11   |
|               | 1853  | 54.65        | 54.19       | +0.46   | 54.49       | +0.16   |
|               | 1854  | 6 12.98      | 12.13       | +0.85   | 12.45       | +0.53   |
|               | 1855  | 30.86        | 30.19       | +0.67   | 30.54       | +0.32   |
| }             | 1856  | 49.36        | 48.37       | +0.99   | 48.74       | +0.62   |
|               | 1857  | 7 7.37       | 6.68        | +0.69   | 7.07        | +0.30   |
|               | 1858  | 25.90        | 25.10       | +0.80   | 25.52       | +0.38   |
|               | 1859  | 44.23        | 43.65       | +0.58   | 44.10       | +0.13   |
|               | 1860  | 8 3.17       | 2.32        | +0.85   | 2.80        | +0.37   |
|               | 1861  | 21.50        | 21.13       | +0.37   | 21.63       | -0.13   |
|               | 1001  | 21.00        | 1           | , 0.01  |             | 0.20    |
| Mean for      | 1856  |              |             | +0.64   |             | +0.26   |
| Paris         | 1851  | 1 5 19.00    |             | +0.34   |             | +0.09   |
|               | 1852  | 37.09        | )           | +0.72   | 1           | +0.45   |
|               | 1853  | 54.73        |             | +0.54   | 1 1         | +0.24   |
|               | 1854  | 6 13.55      |             | +1.42   | 1           | +1.10   |
|               | 1855  |              |             |         | 1 1         |         |
| 1             | 1856  | 6 49.81      |             | +1.44   |             | +1.07   |
|               | 1857  | 7 7.62       |             | +0.94   | 1           | +0.55   |
|               | 1858  | 26.18        |             | +1.08   | 1 1         | +0.66   |
|               | 1859* | 45.06        |             | +1.41   | ! !         | +0.96   |
|               | 1860* | 8 3.45       |             | +1.13   | 1 1         | +0.65   |
|               | 1861  | 22.56        |             | +1.43   |             | +0.93   |
| Mean for      | 1856  |              |             | +1.04   |             | +0.67   |
| Cambr. Eng.   |       | 1 5 19.38    |             | +0.72   |             | +0.47   |
|               | 1852  | 36.68        |             | +0.31   | •           | +0.04   |
| i             | 1853  | <b>55.44</b> |             | +1.25   |             | +0.95   |
|               | 1854  | 6 12.39      |             | +0.26   |             | 0.06    |
| Mean for      | 1853  |              |             | +0.64   |             | +0.35   |

3. There is evidently discrepancy enough between the tables and observation for further investigation. We have

|               |           | Correction of Dr. Gould.   | Correction of Bessel. |
|---------------|-----------|----------------------------|-----------------------|
| Cambridge, En | g., 1853  | + 0.64                     | + 0.35                |
| Greenwich,    | 1856      | +0.64                      | +0.26                 |
| Paris,        | 1856      | +1.04                      | +0.67                 |
| Cambridge, Ma | ss., 1863 | $\stackrel{\cdot}{+} 1.22$ | +0.66                 |

All these numbers have the positive sign, and those referring to Dr. Gould's catalogue are the larger.

4. The mode of investigation which I have now adopted is to compare Bessel's Tabulæ Regiomontanæ with observations of Polaris made at different places during a little more than a century.

<sup>\*</sup> See Erratum, p. 309 of the Annales, Vol. XVI. of the Observations.

I am not confident that I have included all the results which might be collected, although I have made a diligent search for them. But there are results from seventeen different observatories, some of them, as Greenwich, Paris, Dorpat, under several directors; and it is to be noticed that each one of the results in Table I. is derived from more than forty complete transits; in many cases, the number exceeds three hundred. No results have been excluded on account of discrepancy in the final combination of all.

In order to compress Table I. into smaller compass, I have combined several years' work of one observatory, in a somewhat similar manner to that used in §§ 2, 3. In many cases this has been already done by the astronomers themselves. The numbers given above for Cambridge in England, Greenwich, and Paris do not appear in Table I., as the corresponding observations are differently combined.

So far as I conveniently could, I have kept separate the work of different observers. This is not always practicable with the Greenwich, Paris, etc. observations. The names of astronomers in Roman in Table I. are those of the actual observers; those italicized are those of the directors, in cases where several observers employed the same instrument at about the same time.

The notes to Table I. give various details.

I have corrected the results reduced by the nutation-coefficient 8".977 to Peters's value 9".223, so far as the lunar nutation is concerned. The variation of the coefficients of aberration and solar nutation is so mixed with the errors arising from the effect of temperature on the instrument, that the precautions which eliminate the latter will also cause the former to disappear.

Table II. contains the corrections to be added to observations already reduced with the lunar nutation 8".977, to make the results accord with the value 9".223. The part of the correction common to all stars is omitted. The corrections for aberration and solar nutation have not been applied. These, it will be seen at once, are of different signs in different seasons.

The most conspicuous result of the comparison between Bessel's theory and observation is, that the former does, in fact, require a slight correction. This is not remarkable, as it was published about thirty-eight years ago. At that time the great majority of the observations here employed to correct it were not made, and Bessel adopted the wisest course *then* possible. He devoted a considerable portion of

vol. vi. 24

his time for twelve years to the observation of this single star; the result of this was the position for 1820,\*

$$0^{h} 57^{m} 1^{s}.505 + 88^{\circ} 20' 54''.27,$$

which, it will be seen, agrees nearly with observations of other astronomers. For the proper motion he compared this with Bradley's position (Bessel's own *second*† reduction), and from these two determined the A. R. and Dec. for every year from 1750 to 1850.

Like all Bessel's works, this has fully stood the test of time; the correction which now appears necessary can only be deduced by comparison with a great number of observations.

The other computations of the position and proper motion of Polaris to which allusion has been made are Wolfers's in the Tabulæ Reductionum and Dr. Gould's. The first agrees very closely with Bessel's. It is derived from a slightly different and more accurate reduction of Bradley's observations (the one employed in Table I., and cited in the notes), and from the mean of the best observations made about 1830. It does not, however, agree quite so well with observation as Bessel's.

The other one (Dr. Gould's) is also less accurate than Bessel's; both in A. R., for 1855.0, and in proper motion; in the former element its error is about double that of Bessel's, in the latter rather more.

The investigation (Astr. Journal, Vol. VI.) seems hardly complete. We miss in it Bessel's, Argelander's, Carlini's, and Henderson's observations; Airy's Cambridge determination, and, of those made under Struve's direction, the latter half of the Dorpat series (made by Preuss) and Schweizer's Pulcova observations; besides the long series made at Paris under Arago, and several others of less authority.

We must also regret that inaccuracies have crept in. Bradley's place for 1755 is wrongly reduced (by about 2<sup>s</sup> of time) to 1855, and again in another place to 1850; to Piazzi's for 1800, has been added about 3<sup>s</sup>.6, which seems to be the "probable uncertainty" (error verisimilis) of a difference between Argelander and Piazzi. Groombridge's for 1810 has been changed by 4<sup>s</sup>.3 on account (it is stated) of the error of Groombridge's meridian mark. But this error had

<sup>\*</sup> It will be seen in Table I. that I have given separately the results for 1817 and 1824, of the two transit instruments which Bessel then used.

<sup>†</sup> Using as for his own observations Lindenau's nutation.

already been in great part eliminated (for Polaris, at least) by Groom-bridge himself; for, of the ninety-three observations, forty-one\* at least were taken below the pole. Such an error would have been exactly eliminated had one half of the observations been made below the pole.

There are some smaller discrepancies in the reduction to 1850, whose origin it is not easy to trace.

All the larger corrections to be made are of negative sign, and refer to the earlier part of the observations, so that, if they were made, the resulting proper motion would be larger algebraically; while the result for the mean of the dates for which the star's A. R. is correctly given, in the original investigation, would not be much altered, as the following numbers show.

B - G = 
$$0^{\circ}.35 + 0^{\circ}.025$$
 (t -  $1855$ ).  
N - G =  $0.64 + 0.037$  (t -  $1855$ ).

B, G, N, denote respectively Bessel's, Dr. Gould's, and my own  $\dagger$  A. R. of Polaris, for the time t, but referred to the equinox of 1855. In Table I.  $\Delta a$  denotes Bessel's discrepancy from observation;  $\Delta' a$ , Dr. Gould's;  $\Delta'' a$ , my own; C. — O. being taken of an opposite sign to the residuals of §§ 2, 3.

I have used Dr. Gould's formula, depending on the powers of the time. It is not, however, consistent with the trigonometrical computation from his own elements; which would deviate more largely from observation.

The sum of the squares of the discrepancies is,

For B, 12.88; excluding Piazzi and Groombridge, 8.75

" G, 21.91; " " " 15.23

" N, 10.30; " " " 7.24

## 5. REMARKS UPON THE TABLES.

The authorities for the numbers in Table I. are generally well known; and the following remarks would enable any one to derive essentially the same results in detail as I have given.

<sup>\*</sup> Philosophical Transactions for 1810.

<sup>†</sup> I have obtained by least squares, using the residuals in Table I., the correction  $N-B=0^{\circ}.29+0^{\circ}.012$  (t-1855). I did not think it expedient to use either Piazzi or Groombridge here, on account of the doubt about the position of both their instruments. But they would have tended to make the discrepancy of N from G larger.

1755.—Bradley. I have used Peters's reduction of the A.R. of Polaris.

1785. — Maskelyne. The introduction of the known coefficient of nutation into Lindenau's conditional equations for this observer, as well as of L.'s own aberration and parallax, which are very accurate, enabled me to determine the A. R. from 1785, given in the Table with the proper motion + 0°.065 for the same date; which, reduced to 1855, is equal to 0°.082; a quantity sufficiently accurate to show that the progress of wear in the Greenwich transit-instrument would not affect our result seriously.

A trifling change (of about 0°.04) for the better in the representation of Bradley's observations would be made by omitting Maskelyne altogether.

1815, 1820. — Carlini. From the Effemeridi Astronomiche de Milano, 1821, p. 106 of the Appendix.

1817. — Bessel. Observations with the Dollond Transit, 1814 – 1819. Tabulæ Regiomontanæ, p. xliii.

1819.—Struve. Observationes Dorpatenses, III. liii. The latest tables of Bessel referred to are in Volume IV. of the Königsberg Observations. I have added 0<sup>s</sup>.19 to Struve's results, to refer them to his own later determination of the fundamental stars.

1824. — Bessel. Loco modo citato. Observations with the Reichenbach circle, 1820 – 28.

1824, 1832. — Dorpat (Struve and Preuss). See Peters's Numerus Constans Nutationis, p. 18. The quantity w was considered as the correction of A. R. for 1824, according to Struve, and w+w' that for 1832, according to Preuss. Hence the values of  $\Delta a$  are the same as those of w and w+w', with changed signs.

1830. Argelander's A.R. is given by Wolfers in his Tabulæ Reductionum, p. liii. I have no other knowledge about it save that it is manifestly very accurate.

1832.—Pond. I have preferred to employ the observations as given in the annual catalogues from 1829 to 1835, instead of the result of the catalogue for 1830. There is no appreciable difference of results; but there is some obscurity as to the reduction of the earlier observations. The result given for 1825 (1817–26) is (corrected for nutation)  $0^{\rm h}$  58<sup>m</sup> 15<sup>s</sup>.83, which accords well enough with Bessel's value,  $0^{\rm h}$  58<sup>m</sup> 15<sup>s</sup>.49.

1835.—S. Fernando. The mean of the results for 1834 and 1835, of three observers.

has been added to the place of the Tabulæ Regiomontanæ for 1835.

1840, 1850. — Paris. Annales de l'Observatoire Impérial de Paris. Observations, Tome II. p. xxxv. The observations from 1837 to 1845 were reduced to 1840, and those for 1846 – 1854 to 1850.

1840, 1845. — Berlin. The series in Vol. II. of the Berlin Observations, by Encke and Galle, gives for 1843  $\Delta \alpha = +0^{\circ}.06$  (corrected for  $\Delta \nu$ ),

$$\Delta' \alpha = +0^{s}.03$$
,  $\Delta'' \alpha = +0^{s}.18$ .

1842, 1845.—Oxford. Mr. Lucas observed with the old transit instrument, and Mr. Johnson with the new one.

1843. — Doellen. I have not been able to find a copy of the Dorpat observations for 1841 and 1842, which also contain observations by this eminent astronomer.

1848. — Washington. The transit instrument gives, by thirty-seven double transits, 1<sup>h</sup> 4<sup>m</sup> 25<sup>s</sup>.81, and the meridian circle by forty-nine, 1<sup>h</sup> 4<sup>m</sup> 26<sup>s</sup>.92. I have simply taken the mean. The instruments seem both to be affected by temperature.

1855. — Carrington. Double transits alone. Redhill Catalogue, p. xxii.

1858. — Greenwich. Mr. Airy's new Catalogue of 2020 stars gives  $1^h 8^m 3^s.05$ , reduced to 1860. This would give  $\Delta a = -0^s.26$ ; this does not include the result for 1861.

In order to justify the course which has been pursued, in determining the correction to Bessel's A.R., it is necessary to show that Bessel's declination is not largely erroneous. (See my paper in the Memoirs of this Academy, Vol. VIII. pp. 541 et seqq.)

The declination was computed from the place for 1755 in the Fundamenta, compared with Bessel's own for 1820. The correction for 1830 was +0".03 (Argelander in Wolfers's Tabulæ Reductionum, p. liii.) by seven series of observations; that for 1843 is -0".06 (Peters in Struve's Recueil des Memoires, I. p. 201), and for 1850 and 1860 the Greenwich and Paris observations give, as compared with Bessel,

|                | Bessel – Zech. | Observed. | C. — O.                |
|----------------|----------------|-----------|------------------------|
| 1850 Greenwich | 88° 30′ 34″.90 | 35.09     | <b></b> 0".19          |
| 1860 Paris     | 33 47.07       | 47.23     | <b>—</b> 0 <b>.</b> 16 |
| 1860 Greenwich | 33 47 .07      | 47.10     | <b>—</b> 0 <b>.</b> 03 |

No considerable correction seems necessary.

Table II. gives, for the years 1815-1860 inclusive, that part of the correction for the error of Lindenau's nutation, which is not eliminated in the clock-error. In applying it I have been careful to use the mean of the values taken from it for the years of observation, which sometimes extend over a large part of one revolution of the node. For this reason the number in the column  $\Delta\nu$  opposite any given date in Table I. is not usually the result of Table II. for that year.

TABLE I.—Comparison of Computed and Observed Right Ascensions of Polaris.

|      |            |            | • | Com      | puted. | Obs'd. | Δγ     | Δα    | Δ'α   | Δ" α         |
|------|------------|------------|---|----------|--------|--------|--------|-------|-------|--------------|
|      |            |            | h | m        | s      | s      | 8      | 8     | 8     | s            |
| 1755 | Greenwich  | Bradley    | 0 |          | 43.00  | 42.95  |        | +0.05 | +0.69 | -0.61        |
| 1785 | Greenwich  | Maskelyne  | Ĭ |          | 18.20  | 17.66  |        | +0.54 | +1.10 | +0.10        |
| 1800 | Palermo    | Piazzi     |   |          | 25.94  | 25.30  |        | +0.64 | +1.12 | +0.33        |
| 1810 | Blackheath |            |   |          | 39.84  | 37.56  | +0.35  | +1.93 | +2.33 | +1.72        |
| 1815 | Milan      | Carlini    |   |          | 49.66  | 49.32  | , 5.55 | +0.34 | +0.65 | +0.18        |
| 1817 | Königsberg | Bessel     |   |          | 18.15  | 17.72  | +0.28  | +0.15 | +0.47 | +0.01        |
| 1819 | Dorpat     | Struve     |   | 56       | 46.97  | 46.68  |        | +0.29 | +0.59 | +0.17        |
| 1820 | Milan      | Carlini    |   | 57       | 1.50   | 0.65   | +0.56  | +0.29 | +0.58 | +0.18        |
| 1824 | Königsberg | Bessel     | l | 58       | 0.52   | 1.07   | -0.01  | -0.54 | -0.31 | -0.61        |
| 1824 | Dorpat     | Struve     | ١ | 58       | 0.52   | 0.27   | 1      | +0.25 | +0.48 | +0.19        |
| 1830 | Abo        | Argelander | İ | 59       | 31.71  | 31.66  |        | +0.05 | +0.20 | +0.04        |
| 1830 | Cambr. E.  | Airy       | 0 | 59       | 31.71  | 30.88  | 1.     | +0.83 | +0.98 | +0.82        |
| 1832 | Dorpat     | Preuss     | 1 | 0        | 2.85   | 3.44   |        | -0.59 | -0.47 | -0.58        |
| 1832 | Greenwich  | Pond       |   | 0        | 2.85   | 2.31   | l      | +0.54 | +0.66 | +0.55        |
| 1835 | S.Fernando |            |   | 0        | 50.28  | 50.67  | +0.25  | 0.64  | 0.57  | -0.59        |
| 1838 | Edinburgh  | Wallace    |   | 1        | 38.59  | 38.21  | 1      | +0.38 | +0.40 | +0.46        |
| 1840 | Berlin     | Encke      |   | 2        | 11.31  | 10.21  | +0.54  | +0.56 | +0.54 | +0.67        |
| 1840 | Cambr. E.  | Challis    |   | 2        | 11.31  | 10.73  |        | +0.58 | +0.56 | +0.69        |
| 1840 | Greenwich  | Airy       |   | <b>2</b> | 11.31  | 10.93  |        | +0.38 | +0.36 | +0.49        |
| 1840 | Paris      | Arago      | 1 | 2        | 11.31  | 11.10  | 1      | +0.21 | +0.19 | +0.32        |
| 1842 | Oxford     | Lucas      |   | 2        | 44.44  | 45.23  |        | 0.79  | -0.85 | 0.66         |
| 1843 | Pulcova    | Schweizer  |   | 3        | 1.17   | 1.91   |        | -0.74 | -0.82 | -0.61        |
| 1843 | Dorpat     | Döllen     |   | 3        | 1.17   | 2.06   | -0.10  | -0.79 | 0.87  | -0.65        |
| 1845 | Berlin     | Galle      |   | 3        | 34.94  | 36.31  | -0.42  | 0.95  | -1.07 | -0.79        |
| 1845 | Oxford     | Johnson    |   | 3        | 34.94  | 35.26  |        | -0.32 | 0.44  | 0.16         |
| 1845 | Greenwich  | Airy       |   | 3        | 34.94  | 34.35  |        | +0.59 | +0.47 | +0.75        |
| 1848 | Washingt'n | Maury      | 1 | 4        | 26.42  | 26.37  | 1      | +0.05 | -0.13 | +0.25        |
| 1850 | Greenwich  | Airy       |   | 5        | 1.30   | 1.26   | l      | +0.04 | -0.19 | +0.27        |
| 1850 | Cambr. E.  | Challis    |   | 5        | 1.30   | 1.73   |        | 0.43  | 0.66  | -0.20        |
| 1850 | Paris      | Arago      |   | 5        | 1.30   | 1.18   |        | +0.12 | -0.11 | +0.35        |
| 1855 | Redhill    | Carrington |   | 6        | 30.54  | 31.27  |        | -0.73 | -1.08 | -0.44        |
| 1858 | Greenwich  | Airy       |   | 7        | 25.52  | 25.84  |        | 0.32  | -0.74 | +0.01        |
| 1859 | Paris      | Le Verrier |   | 7        | 44.10  | 44.90  |        | -0.80 | 1.25  | -0.46        |
| 1863 | Cambr. M.  | Safford    | 1 | 8        | 59.68  | 60.34  |        | -0.66 | -1.22 | 0.26         |
|      |            | 1          |   |          |        | 1      |        |       | l     | 1            |
| ·    |            |            |   |          |        |        |        |       |       | <del>`</del> |

| Year. $\Delta \nu$ | Year. Δν    | Year. Δν    | Year. Δν    |
|--------------------|-------------|-------------|-------------|
| s                  | 8           | 8           | s           |
| 1815 -0.02         | 1827 -0.44  | 1839 + 0.58 | 1851 -0.26  |
| 1816 + 0.16        | 18280.55    | 1840 + 0.51 | 1852 0.05   |
| 1817 + 0.33        | 1829 —0.59  | 1841 + 0.38 | 1853 +0.16  |
| 1818 + 0.46        | 1830 —0.56  | 1842 +0.20  | 1854 + 0.35 |
| 1819 + 0.54        | 1831 0.47   | 1843 0.00   | 1855 + 0.50 |
| 1820 + 0.56        | 18320.34    | 18440.20    | 1856 + 0.60 |
| 1821 + 0.52        | 18330.14    | 1845 0.38   | 1857 + 0.63 |
| 1822 + 0.41        | 1834 +0.06  | 1846 -0.52  | 1858 + 0.59 |
| 1823 + 0.26        | 1835 + 0.26 | 1847 —0.60  | 1859 + 0.48 |
| 1824 + 0.08        | 1836 + 0.42 | 18480.62    | 1860 + 0.32 |
| 1825 —0.11         | 1837 + 0.53 | 1849 0.54   |             |
| 1826 0.28          | 1838 +0.59  | 1850 -0.43  |             |

TABLE II.

On a Process of Organic Elementary Analysis, by Combustion in a Stream of Oxygen Gas. By C. M. WARREN.

The process in general use for ultimate organic analysis had seemed to me so nearly perfect as to leave little room for any very marked improvement. Like all other processes of analysis, however, it has its own peculiar sources of error, inherent in the nature of the substances employed, and in the manipulations to be performed. But these appear to have been reduced to a minimum; so that, with great care and the necessary skill, there can be no reason to doubt that that process, with the various modifications which have been proposed to meet special cases, is capable of affording as accurate results, in a majority of instances, as can, perhaps, be claimed for any other analytical process. Nevertheless, there are instances, and they are doubtless numerous, where so satisfactory a solution of the question which may be under consideration as would be highly desirable, cannot be attained by that process. It was after repeated unsuccessful efforts, in a case which appeared to be of this kind, that I was led to conceive the idea of making the combustion in oxygen gas alone; and to devise the method which I am about to describe.

Were it not for the danger of explosions in the combustion tube, the occurrence of which would, at least, render its use fruitless of good results, the employment of pure oxygen, as a combustion agent in analysis, would seem, of all substances, the one most naturally suggested. This apparent difficulty is probably the chief reason it has not long ago been brought into general use; its employment since the time of Prout, so

far as I am informed, having been mostly confined to the combustion of the residual carbon of highly carbonaceous substances, after the other decomposition products, containing the hydrogen, had been burnt at the expense of oxide of copper.

By a very simple device I entirely obviate the danger of explosion; viz. the combustion tube is closely packed with asbestos, or other inert substance,\* and yet so loosely as to leave free passage for gases through the interstices. The packing of the tube requires some care. This, however, may be readily accomplished, giving great uniformity to the mass of asbestos, by having the latter carefully broken into small, loose pieces, which are gradually added to the tube, and arranged in position by means of a stiff iron wire. Little attention need be had to the packing of the centre of the tube, as this will come right of itself, if the packing against the sides is properly done. It will be found convenient and expeditious to turn the tube continuously in the hand, and cause the end of the iron rod to follow around against the sides of the tube, placing the asbestos, by gentle taps, alongside its inner surface, so that only very small open spaces may be seen.

In the experiments which I have made I have generally had about ten or twelve inches in length of the tube filled with asbestos. As the combustion takes place within a very short space, it seemed at first that the tube might be reduced considerably below the ordinary length; it was found, however, that shortening of the tube below a certain limit made it difficult to control the distillation of volatile substances and prevent too rapid combustion; it being essential in this, as in other processes, that the combustion should proceed slowly, and with a good degree of regularity; otherwise it would be difficult to regulate the supply of oxygen to meet the demand of the burning substance. By

<sup>\*</sup> I have used only asbestos in my experiments thus far, and in every instance with perfect success. Quartz sand, selected with care as to the size of the grains, had suggested itself, on account of greater convenience in filling the tube, as it would properly arrange itself on simply being poured into the tube. It would, however, be liable to the objection, that any jarring of the tube, while lying upon the combustion furnace, would be likely to settle the particles more closely together, and form a channel along the top, in which an explosion might take place which would spoil the analysis. I therefore prefer asbestos to anything which I have thought of; and any apparent inconvenience in preparing a tube with this substance will pass into insignificance, if the precautions which I advise for protecting the tube from breakage are observed, as then the same tube may be made to last for a long time.

having the column of asbestos of considerable length, the anterior end of which only is ignited, the substance, if volatile, becomes diffused through a large space, and the distillation thereby easily controlled; as only a small portion of the substance need then be heated at a time. Doubtless a shorter tube would answer equally well for many non-volatile substances. It will be observed that the asbestos packing is but another application of the principle involved in the use of wire gauze in Davy's safety-lamp.\*

In order to obtain perfect control of the analysis, and to be always certain that the requisite quantity of oxygen is being admitted, I have adopted certain simple expedients, enumerated below, which have been found fully adequate to that end.

1. The distillation of the substance, if volatile, is effected by means of a bar of copper, placed over and attached to one of Bunsen's burners, as shown at a, in the accompanying figure.

This bar, having first been brought to the maximum temperature which the lamp is capable of producing, is placed near or under the bulb containing the substance; applying that part of the bar nearest or most remote from the flame, or an intermediate point, according to the temperature required.

The steadiness of the heat thus applied, and the facility with which it may be regulated, by simply moving the bar, render it decidedly preferable to any other means which I have employed for that purpose. I had for a long time used such a bar for the same purpose in the old process, with extreme satisfaction. In some cases a bar of copper laid on the combustion furnace, tone end projecting into the flame by which

<sup>\*</sup> It has occurred to me that my safety-tube may serve as the basis of a more simple and equally accurate process for the analysis of gases, by gradual combustion, instead of explosion; in which weighing would take the place of measurement. I propose, at an early day, to study this question by a series of experiments.

<sup>†</sup> As there are those, and probably there are many, who still persist in the use of charcoal in place of the more modern gas furnaces for generating heat for combustions, I desire here to say that I have in use one of Baumhauer's gas furnaces, procured a few years ago from Luhme & Co., in Berlin, which seems to me to have no fault. It is impossible for me to conceive what objection one could have to it, unless it be that a naked tube might become overheated along the bottom; and this would be a valid objection if the remedy were not so simple. If the tube be taid in a trough of sheet iron (brass is objectionable, in my process, on account of its obscuring the tube with oxide of zinc), with a thin layer of asbestos between, and fastened together with wire, no harm can ever occur from overheating. A

the tube is being heated, and the other end raised and extending towards the substance, has been found to answer a good purpose.

2. In the case of volatile bodies (I have not yet analyzed any others by this process), I have found the combustion to proceed most satisfactorily when, having first heated about four or five inches of the anterior portion of the tube, which includes the oxide of copper, and started the flow of oxygen, I apply the heated bar to the bulb containing the substance, and immediately expel the whole of the liquid, - which becomes at once absorbed by the asbestos, - and then, if necessary, gradually move the heated bar forward, driving the substance towards the ignited portion of the tube, until it shall have reached that point in the tube where the temperature is just sufficient to cause the oxygen to take up the vapor in suitable proportion; indicated by the bubbles of oxygen and carbonic acid, as will be described below: - a point as easily found as to find, in the old process, the requisite temperature for proper distillation of the substance. When this is accomplished, which will occupy but a short time, the heat in front of and behind the substance being constant and uniform, no further manipulation of the heat is re-

tube of Bohemian glass, thus protected, may be used for a large number of analyses; and, indeed, become almost a permanent fixture upon the furnace. The asbestos prevents the glass and metal from adhering together,—which is probably the chief or only cause of breakage of wrapped tubes,—so that sudden cooling and re-heating may take place with perfect security. It is important that the iron trough should not extend much backward of that part of the tube where it is desired that the combustion should take place, so that the temperature of the principal part of the column of asbestos may remain under the control of the operator, by means of the heated copper bar, or otherwise.

Independent of the use of a metallic bar, as described above, or any novel appliance, the heat can be regulated by this furnace with as great, or even greater nicety than by the use of coal. The partitions in this furnace, between the cocks, are two inches apart; so that the gas from one of the jets ignites about two inches of the tube. To rely, therefore, alone upon the cocks for regulating the heat in burning the substance, would doubtless often lead to bad results; but the heat may be made to approach the substance in the most gradual manner, — next to that of conduction by a metallic bar, — by making use of a piece of thin brass plate, about two inches long, and half an inch wider than the top of the furnace, the edges of which are turned down against the sides.

If this plate is laid on the wire gauze covering the furnace, and pressed down so as to fit closely enough to prevent the gas from igniting under it, the gas escaping from the cock underneath may all be made to burn at one end of the plate, and to extend the heat along the tube as gradually as the plate itself is capable of being moved.

quired; the supply of oxygen only requiring attention. In the ordinary way, on the contrary, in which the heat is applied only on one side of the substance, the latter, if volatile, is constantly changing position backward in the tube, necessitating a corresponding movement of the heat in the same direction; which requires constant care and considerable skill.

This procedure—referring to the immediate expulsion of liquid from the bulb, etc. — implies that that portion of the tube immediately forward of the bulb should not already be too warm, which might easily be the case with a body of very low boiling-point. It would then be necessary to expel the substance from the bulb no faster than the oxygen would absorb it in the proper proportion; which, as experience has shown, may be easily accomplished.

With a body of extreme volatility it may be also necessary to place a dish containing pieces of ice under the bulb; as even the temperature of the surrounding air might in such a case cause the substance to pass forward too rapidly.

3. The oxygen is admitted through Liebig's potash bulbs containing sulphuric acid; and the carbonic acid formed is absorbed by similar bulbs with potash; to which is attached a tube filled with soda-lime and chloride of calcium, as recommended by Mulder,\* to take up any traces of carbonic acid which may escape absorption in the bulbs, and the trace of moisture which is invariably carried forward from the latter. Special care should be taken to select both sets of bulbs with the view to have the openings in the one as nearly as may be of the same size as those of the other, so that the bubbles of oxygen, considered as representing volumes, entering the sulphuric acid bulbs, may be readily compared with the bubbles or volumes of carbonic acid entering the potash bulbs; these bubbles may then serve as a valuable index by which to regulate the supply of oxygen. Especially is this true in cases where the composition of the body to be analyzed is pretty nearly known, as then the number of bubbles of oxygen required for every bubble of carbonic acid produced may be readily calculated.

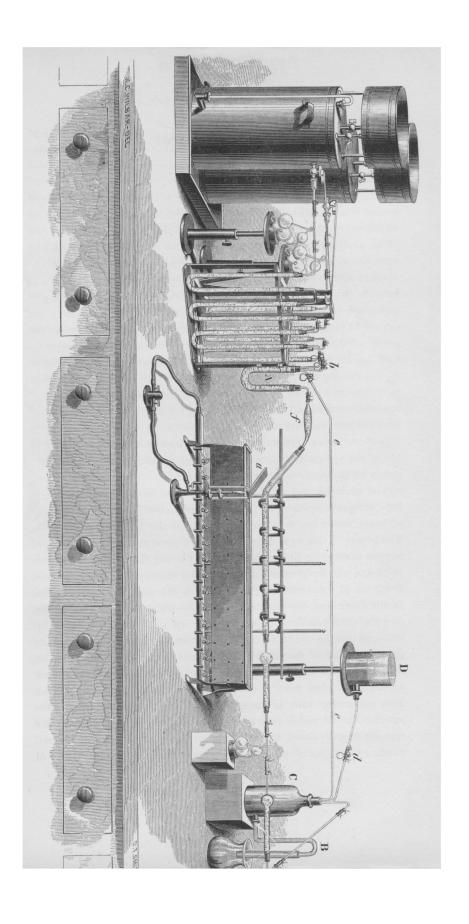
But as it is, in any case, advisable to conduct the experiment so that there shall always be an excess of oxygen passing unabsorbed through the potash bulbs, and as this excess would seldom be large even

<sup>\*</sup> Liebig and Kopp's Jahresbericht, 1858, p. 588.

if a sufficiency of oxygen were admitted to burn the most richly hydrogenized body known, it may generally be well to admit enough for such a case.

The volume of oxygen actually consumed in burning the lightest liquid known — probably of the formula C<sub>8</sub> H<sub>10</sub> — which I have separated from petroleum, and which contains a larger percentage of hydrogen than any other non-gaseous body, as compared with the volume of carbonic acid formed, is as 1.62:1; the fraction representing the oxygen which is taken up by the hydrogen of the body, and which of course becomes condensed and disappears from the volume of carbonic acid. In burning this body with just the equivalent quantity of oxygen, - assuming that the combustion would be complete under such circumstances, - we should have one bubble or volume of carbonic acid entering the potash bulbs for every 1.62 bubbles or volumes of oxygen entering the sulphuric acid bulbs. A sufficient excess of oxygen would be secured in this case, and a simple ratio obtained, if 2 bubbles of oxygen were to be admitted for 1 bubble of carbonic acid appearing in the potash bulbs. The case would then be further simplified by having the openings in the sulphuric acid bulbs of such size as would give bubbles twice as large as those from the potash bulbs; as then, when the bubbling should be equally rapid in both, the relation between the volumes of the gases would still be maintained, viz. 2 vols. of oxygen to 1 vol. of carbonic acid. Such bulbs would be highly desirable, but would probably have to be made expressly for the purpose.

4. As an additional control over the supply of oxygen, and serving also as a temporary safeguard against the escape of incompletely oxidized substance, in case of too rapid distillation, with an insufficient flow of oxygen, I have two or three inches in length of the tube filled with coarse, strongly ignited oxide of copper, placed in front of the asbestos, and this followed by a plug of the latter substance to keep it in place, and prevent the formation of a channel along the upper surface of the oxide of copper. The tube itself being laid in an iron trough, as above described, with the upper half of the tube exposed, the oxide of copper is heated in such a manner that any reduction would be readily observed at the end in contact with the asbestos. In this manner it serves as a valuable indicator, by which to determine, at a glance, whether the flow of oxygen is sufficient. It will rarely happen that any reduction of the oxide of copper will take place. I have, however, in some of my earlier experiments, with too short a column of asbestos,



and ill-adapted bulbs, had so much of the oxide of copper reduced that combustible gasses passed through the absorbing apparatus; and in one instance, when the unabsorbed gases were collected, the quantity of combustible gas was so considerable as to form, with the oxygen collected with it, - which of course came forward at an earlier or later stage of the process, - an explosive mixture. Having seen no indications that any other than gaseous bodies escaped the combustion tube in such a case, it occurred to me that such an analysis might be saved by collecting the gas over mercury, and, at the close of the combustion, before detaching the absorbing apparatus, conducting it a second time through the combustion tube.\* As a matter of economy, also, in the saving of the excess of oxygen, when a considerable number of analyses are to be made, this idea seemed to recommend itself; as the oxygen would, at the same time, become purified from any traces of combustible matter which might be present, and could then safely be collected as pure oxygen, and finally transferred to the oxygen gasometer.

I therefore constructed for this purpose the apparatus which is represented in the background of the accompanying figure as attached to the anterior end of the absorption apparatus. At the close of the combustion, when only pure oxygen appears to enter the potash bulbs, the flow of oxygen is interrupted; the communication with that portion of the drying apparatus which is back of the short U tube, A, is closed at b; and the tube B— which is movable in the cork—turned up.† The joint at c is then disconnected; the end leading to the receiver C tightly closed with a piece of glass rod; and a communication established between the absorption apparatus and another receiver containing water,—not shown in the figure,—for collecting the pure oxygen. On opening the spring-clip d (the more modern form, which is provided with a fine screw, is excellently well adapted for this purpose), the mercury will flow from the reservoir D into the receiver C, and force

<sup>\*</sup> As the time consumed in an experiment is so short, and the quantity of combustible gas present, if any, so very small, and that mixed with a very large quantity of oxygen, it is not improbable that the gas might as well be collected over water; as the quantity which could be absorbed by the water in so short a space of time would probably be inappreciable.

<sup>†</sup> That this tube may not operate as a siphon, the outer limb is formed by attaching, near the bend, a flexible tube, of larger bore than that of the glass tube. This flexible tube is preferable to glass, on account of the readiness with which it adapts itself to any change of position of the glass tube, by which it may always project into the receiver underneath, and prevent waste of mercury.

the gas through the capillary tube ee; thence through the short U tube A, containing chloride of calcium, to the combustion tube and absorption apparatus; and the gas is finally collected over water in the receiver provided for that purpose.

The introduction of a longer column of oxide of copper would probably accomplish the same purpose with less expense; but neither expedient can be regarded as essential to the process. As the saving of an analysis by the use of a longer column of oxide of copper would only be occasional, the additional heat required, and consequent discomfort occasioned by its continued use, would hardly be compensated for. So that, while I would not, therefore, recommend the use of an additional quantity of oxide of copper, I would also discard the other expedient of collecting the gas over mercury or water, etc., unless the saving of the surplus oxygen, together with the additional security afforded, should be considered of sufficient importance to recommend it. As the passing through of the gas the second time requires no attention after it is once started, and occupies but a short time, during which the operator may attend to anything else, I much prefer, for myself, to retain in use that part of the process.

5. Some other less important peculiarities in the construction and use of the apparatus will now be noticed, in connection with some remarks on the performance of the analysis.

The posterior end of the combustion tube, as seen in the figure, is bent obliquely upward, as in the common form, except that, instead of being drawn out to a point, it is left of the full size of the tube. The object of this form is to prevent, in a great measure, the escape of oxygen during the time occupied in introducing the substance for analysis; and also for greater convenience and security from loss in the performance of this operation; especially in the case of volatile liquids. In the latter case, the neck of the bulb — which has previously been provided with one or more scratches on its side near the end - is introduced into the end of the combustion tube, and broken off by pressure against the side of the tube; the bulb itself is then allowed to drop in, and the end of the tube immediately closed with a perforated cork containing a glass tube, f, connecting it with the drying apparatus. This connecting tube is constructed of hard Bohemian glass; the anterior end of which is drawn out to a short, blunt point, and the opening nearly closed in the blowpipe flame, to the size of a small needle; the object of which is, to increase the rapidity of the flow of

oxygen at that point, and thereby diminish the liability to loss from diffusion of gases or vapor backward into the drying apparatus, which is always too liable to occur when the posterior end of the combustion tube is not sealed.

As an additional precaution against loss from this source, this connecting tube is packed with asbestos in the same manner as the combustion tube; and during the combustion is heated with one of Bunsen's burners. In case vapor of the substance should reach this tube, notwithstanding the above precaution against it, it could not reach the drying apparatus as such; but would be immediately decomposed, and the carbonic acid formed would at least stand a good chance of being carried forward, and prevent a loss in the determination of the carbon. The heating of this connecting tube may be superfluous for the object above described (a point which I have not yet taken the time to determine); but it certainly has the good effect of heating the oxygen, and thus preventing the condensation of liquid at the cork in the end of the combustion tube.

In the performance of an analysis, the first step should be to expel the moisture from the combustion tube, while hot, by passing through it, for some time, a stream of dry air from the gasometer.\* The tube should then be filled with oxygen, before the substance, if volatile, is added; as otherwise particles of unburnt substance might escape during the displacement of the air, and occasion loss. The absorbing apparatus, having been previously weighed, is then attached, and, if the excess of oxygen employed is to be saved, the oxygen again admitted to expel the air from the absorbing apparatus. The connection is then made with the receiver C, if used, and the tightness of the joints tested by turning down the tube B, so as to partially exhaust the apparatus.

<sup>\*</sup> The necessity for this may be entirely obviated, after the first analysis, and much time saved and uncertainty avoided, by connecting the anterior end of the combustion tube, at the close of a day's operations, with a set of stationary drying tubes of ample capacity, which may stand back of the furnace out of the way, communication with which is established by means of a flexible tube. Or, better, a movable tube may be attached by means of a screw to the opening in the top of the gasometer, extending to the top of the upper reservoir, so that water cannot enter, and then, by simply turning the cock underneath, communication would be opened between the surrounding air and the combustion tube, through the intervening drying apparatus. At the close of work the anterior end of the combustion tube should then be tightly corked, the fire extinguished, and the tube allowed to cool in dry air. It would thus be always ready for immediate use.

If found tight, as indicated by the liquid in the potash bulbs, the tube B is again turned up, and the substance then introduced in the manner above described. A very slow stream of oxygen is now admitted; the tube B again turned down till the level of mercury in this tube shall be half an inch to an inch below the level of mercury in the receiver C; and from time to time during the combustion the position of this tube is adjusted so as to preserve about this difference between the levels of the mercury, or at least so as to prevent the mercury in the tube from ever rising above that in the receiver.

In this manner the mercury, instead of offering resistance to the passage of gas from the combustion apparatus, and thus increasing the internal pressure upon the joints, which would be objectionable, actually operates advantageously by producing partial exhaustion, and thus diminishing the internal pressure upon the joints, and consequently the liability to leakage. The distillation of the substance is now commenced, and conducted as previously detailed above. So soon as condensation of moisture appears in the neck of the chloride of calcium tube, indicating that combustion has commenced, the flow of oxygen may be gradually accelerated to keep pace with the progress of the combustion, as indicated by the bubbles in the potash bulbs. When the burning of the substance seems to have been completed, heat is gradually applied, for a short time, along the whole length of the column of asbestos, to obviate the possibility of any loss from unburnt substance.

The absorbing apparatus may be weighed filled with either oxygen or air; for myself, I prefer the latter, as, on the whole, more convenient and less liable to lead to error. At the close of the analysis, therefore, I expel the oxygen from the apparatus by admitting air from the airgasometer,\* saving for further use the oxygen which is expelled during

<sup>\*</sup> The oxygen-gasometer and the air-gasometer each having a separate drying apparatus, the time consumed in changing from one to the other is very much shortened, as the necessity for displacement of the oxygen or air—as the case may be—which is contained in the drying apparatus is avoided. Each drying apparatus consists, 1st, of Liebig's bulbs, containing sulphuric acid; 2d, of a U tube, 15 inches high (nearly 3 feet of tube), filled with soda-lime for carbonic acid; and, 3d, of two such U tubes (5 to 6 feet of tube), filled with chloride of calcium. The object in using drying tubes of such large dimensions is to avoid the necessity of too frequent renewal. The gasometers stand in a pan of copper, which is provided with an outlet to the sink, so that they may be filled without disconnecting from the drying apparatus; thus giving a degree of permanence to the apparatus and saving some labor.

the first five or six minutes. Thus far I have applied this process only in the analysis of volatile hydrocarbons of the formula  $C_n H_{n-6}$ ;  $C_n H_{n+2}$ , etc.\* As a mixture of the vapors of these bodies with oxygen is highly explosive, a more severe test of the safety of the process could not be applied.

In every experiment which I have made, the combustion has proceeded as quietly as if burning in the open air. The results obtained are extremely accurate and uniform.

Although the bodies which I have analyzed represent but a single class of organic substances, I can see no reason to doubt that the process will apply equally well in the generality of cases.

If this view be corroborated by actual experiment, the process can hardly fail to supplant the common methods; if for no other reasons than its greater convenience, economy of time, avoidance of excessive heat, neatness, etc.; while, as regards accuracy of results, it will, at least, not be found inferior to the other methods; but, on the contrary, I think preferable, as affording greater security against failures and errors from accidental causes.

Having obtained such satisfactory results in the cases referred to, and being prevented by other important work, to which the study of this process is only incidental, from pursuing the subject further at present (except so far as I shall have occasion to use the process in my other investigations), I have thought it advisable to present the process to the Academy as it now stands. I hope, however, before long to be able to resume the work, with the view to determine, by experiment, the extent of its applicability as a general method, and will report the results to the Academy.

<sup>\*</sup> In an analysis of amyl-alcohol, made in my laboratory by my friend Mr. Storer, for the sake of familiarizing himself with the process,—it being his first analysis by this apparatus,—the following result was obtained.

|           | E | xperiment. | Theory. |  |
|-----------|---|------------|---------|--|
| Carbon, . |   | 68.53      | 68.18   |  |
| Hydrogen, |   | 13.63      | 13.64   |  |